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Synthesis and characterization of polyurethane composites of wood waste and polyols from chemically recycled pet

Marcia Fornasieri^a, Juliana Weiller Alves^b, Edvani Curti Muniz^b, Adhemar Ruvoilo-Filho^c, Harumi Otaguro^c, Adley Forti Rubira^b, Gizilene Maria de Carvalho^{b,*}

^a Universidade Norte do Paraná – UNOPAR, Araçongas-Pr, Departamento de Química, Campus Universitário de Araçongas, Brazil

^b Universidade Estadual de Maringá – UEM, Maringá-Pr, Departamento de Química, Grupo de Materiais Poliméricos e Compósitos, Brazil

^c Universidade Federal de São Carlos – UFSCar, São Carlos, SP, Departamento de Química, Grupo de Processamento e Propriedades em Polímeros, Brazil

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ABSTRACT

Polyurethane/wood-based composites were synthesized with wood waste from furniture companies of the north of Parana State and polyols obtained from chemically recycled poly(ethylene terephthalate) (PET) and commercial polyols. Wood was chemically modified (maceration with peracetic acid) to provide phase adhesion. The composites were prepared with proportions of macerated wood waste (0–25% m/m) and fixed amounts of polyols and toluene diisocyanate (TDI). FTIR and SEM analysis indicated adhesion of wood with polymer matrix. The relative Young's modulus and relative tensile strength of the composites confirm this result, indicating effective load transfer from the matrix to the dispersed phase. No significant improvement in the thermal stability of the composites is observed.

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1. Introduction

Natural fibers have been largely used to produce composites or as reinforcers of thermoplastic and thermoset polymer matrixes in textile, car, packaging, civil construction industry applications, and so forth [1–5]. According to Mano, this growing interest is due to the low cost and biodegradability of these raw materials and the good mechanical properties that they impart to composites [6]. The Brazilian association of the furniture industry, ABIMOVEL, estimates that the number of furniture companies in Brazil is around 50,000, including formal and informal businesses. The furniture pole of Araçongas, in the north of Parana State, is the second largest in Brazil and the largest in Parana. Approximately 200 tons of wood wastes are produced per day in the processing of solid wood or reconstituted wood panels. Currently, these residues are used in energy or charcoal production [7]. The generation of waste is a natural consequence of wood processing. Among these waste, sanding dust and sawdust deserve special attention, as low density materials require greater storage room and cause major pollution problems if they are not properly disposed [8,9].

Considering the growing interest in the use of natural fibers in the production of composites with different polymer matrixes, wood wastes are an alternative source of fibers, thus reducing

the environmental impact of the large amounts of waste produced by the furniture industry [10]. For the synergy of the properties of the composite components their respective phases must present adhesion, which can be provided by fiber surface modification and/or the use of compatibilizing agents. Fiber surface can be modified by different processes [11,12]. Some studies have demonstrated that chemical treatments reduce fiber impurity, increase the effective fiber surface area, and significantly improve interfacial matrix/fiber adhesion, thus reducing the tendency of dimensional variation of wood with humidity [13,14]. This is due to the binding of hydroxyls to other components, which are not available to interact with water molecules [15,16]. The combination of properties of industrial waste wood-based fibers and highly versatile polymers, as polyurethane, can be used to produce composites with specific properties. The nature of the fibers, which are rich in hydroxyls, suggests that they are particularly interesting in polyurethane-based systems, in which the hydroxyl groups at the fiber can form chemical bonds with diisocyanate $\text{N}=\text{C}=\text{O}$ groups [16–18].

A large variety of polyols are used in the production of polyurethanes. The polyols obtained by way of glycolysis of poly(ethylene terephthalate) (PET) (polyester polyols) have been increasingly used due to the possibility of obtaining products with different molar weights and physical characteristics as a function of the glycol content, the stoichiometric ratio of reagents, and the reaction conditions [18,19].

* Corresponding author. Tel.: +55 44 3011 3687; fax: +55 44 3011 4125.

E-mail address: gmc Carvalho@uem.br (G.M. de Carvalho).

This work aims at synthesizing polyurethane/wood composites from waste materials (wood, and polyols issued from partial degradation of PET by ethylene glycol). The composites were characterized by chemical, thermal, morphological, and mechanical analyses.

2. Experimental

2.1. Wood preparation

Composites were made from wood waste coming from the Furniture Park of Arapongas, in the north of Parana State, kindly supplied by the Centro de Tecnologia em Ação e Desenvolvimento Sustentável – CETEC. The samples were ground in a Marconi MA 340 mill (Macro vertical mill with a rotor of fixed blades) and sorted out in a “Produtest” Model “T” vibrating machine with decreasing sieve meshes of 0.71 mm, 0.42 mm, 0.35 mm, 0.25 mm, 0.106 mm, and remains. Particles retained through meshes 0.42 mm (26%) and 0.106 mm (14%) were sorted out for sample preparation, as these sizes were in larger amounts than the others. After that, as-prepared samples were washed with distilled water for 1 h under constant stirring at 80 °C, and dried in oven at 100 °C until constant weight was obtained.

2.1.1. Wood maceration

Dried wood samples were immersed in glacial acetic acid, 120-volume hydrogen peroxide, and water at the percent rate of 50:38:12 for 12 h under continuous stirring at 60 °C. Afterward, the fibers were washed with water until pH of nearly 7 and dried in oven at 60 °C for 24 h. Thereafter, the sample was identified by label W-OH. TGA analysis indicated moisture percentage of 3.4 in the W-OH sample. Microscopic and spectroscopic analyses were the technique used to characterize the W-OH.

2.2. Polyol characterization

The product of partial degradation of PET by ethylene glycol (named PDG) ($M_n = 905$ g/mol) was prepared according to Viana [20]. Polyethylene glycol (PEG 4000) ($M_n = 4000$ g/mol) and PDG were characterized on basis of their hydroxyl content (I_{OH}) [21] and acidity content (I_{COOH}) [18].

To determine the acidity content (I_{COOH}), 1–2 g of PEG 4000 or PDG was dissolved in 25 mL of acetone and titrated with 0.5 M potassium hydroxide in alcoholic solution (KOH, Nuclear) previously standardized with potassium biphthalate using 1% phenolphthalein in alcohol as an indicator. The acidity content was calculated applying following equation:

$$I_{COOH} = \frac{V \times 56.11 \times M}{m_a} \quad (1)$$

where I_{COOH} is the acidity content in mg KOH/g, V the volume of KOH solution consumed in titration, M the concentration of the KOH solution in mol/L and m_a is the sample mass in grams.

2.3. Preparation of PU-TDI composites with macerated wood

2.3.1. Chemical modification of wood

W-OH was placed in a 250 mL three-neck round-bottom flask, equipped with a magnetic stirrer, thermometer, condenser, and soaked with 30 mL of ethyl acetate at 75 °C for 30 min under continuous stirring. Toluene diisocyanate (TDI) was added into the flask and the reaction was continued for more 60 min at the same temperature under continuous stirring. After that, the sample was filtered and washed three times with ethyl acetate and dried at 100 °C until constant mass. Dried wood sample (W-NCO) was characterized by FTIR and the isocyanate content (%NCO) was determined by ASTM-D2572-80 [22].

2.3.2. Synthesis of polyurethane/wood composites

All polyurethane/wood composites were synthesized using 4 mols of TDI, 0.5 mol of PEG 4000, and 0.275 mol of PDG. The amounts of wood in the composites ranged from 0% to 25% in relation to the total composite mass (Table 1). A 250 mL three-neck round-bottom flask, equipped with a magnetic stirrer, thermometer, condenser, was used as a polymerization reaction vessel. The polymerization reaction was carried out in a oil bath at constant temperature. The W-OH and 30.0 mL of ethyl acetate was introduced into the flask and the system was heated to 75 °C, under stirring. Then, TDI was added slightly with a dropper and the reaction mixture was left to react for 60 min to obtain NCO-terminated wood. After that, both PEG 4000 and PDG were also added and the reaction was kept for more 20 min. The obtained material was represented by the following PUX form, where X indicates the percent of macerated wood in the composites. It was poured onto a Teflon plate and the ethyl acetate was evaporated at room temperature until weight constant (24 h). PU0 was obtained in the same way of the PUX, but it does not contain macerated wood. Afterward, both the composites and the PU0 samples were cut into appropriate forms for characterization.

2.4. Characterization techniques

2.4.1. Fourier-transformed infrared photoacoustic spectroscopy (FTIR-PAS)

Both the wood samples and the composites were analyzed by infrared spectroscopy in a photoacoustic mode with use of a BOMEN MB-100 apparatus. A total of 512 scans were run to reach resolution of 2 cm⁻¹ for each spectrum.

2.4.2. Thermogravimetric analysis (TGA)

The thermal stability of the samples was determined on a NET-ZSCH-STA 409 PSPG equipment with a heating rate of 10 °C/min and nitrogen stream of 20 mL/min.

2.4.3. Scanning electron microscopy (SEM)

Sample morphology was analyzed on a SHIMADZU SS-550 Superscan. The sample was cracked after the immersion in liquid nitrogen for 10 min. Before observation by SEM, the samples were sputtered with a thin layer of gold-on the respective cracked sections. SEM micrographs were taken at different magnifications applying an accelerating voltage of 40.0 kV and a current intensity of 30.0 mA.

2.4.4. Mechanical tests

Stress-strain tests were performed on an EMIC DL2000 equipment interfaced to a personal computer with the mechanical assay control software MTest version 2.00. The samples were obtained according to standard ASTM D638 (typeIV) with initial gage length of 40.0 mm, width of 4.0 mm, and varying thicknesses. The tension tests were conducted by applying a loading force of 2000 N and a constant speed of 5 mm min⁻¹. Tensile strength (σ) and deformation (ϵ) curves were plotted. The results were obtained as the average over at least five measurements.

Table 1
Proportion of wood, TDI and polyols.

Sample	Macerated wood (%)	TDI (mL)	PDG (g)	PEG 4000 (g)
PU0	0	1.74	0.65	5.0
PU7.5	7.5 (0.56 g)	1.74	0.65	5.0
PU10	10 (0.74 g)	1.74	0.65	5.0
PU15	15 (1.11 g)	1.74	0.65	5.0
PU20	20 (1.48 g)	1.74	0.65	5.0
PU25	25 (1.85 g)	1.74	0.65	5.0

3. Results and discussion

3.1. Wood modification

The chemical treatment of wood with peroxide in acidic medium aimed to improve fiber/polymer adhesion and promote the exposure of the hydroxyl groups to serve as binding sites for reaction with TDI. This treatment extracts fiber surface substances such as fats, waxes, and part of the hemicellulose and lignin [11,12,17]. Fig. 1 shows the SEM micrographs of wood before and after chemical modifications.

Fig. 1a and b shows the SEM micrographs of untreated wood (particles retained in both the 0.42 mm and the 0.106 mm sieves). No morphological differences were observed in the micrographs, allowing that these two samples were mixture before maceration. Fig. 1c and d shows the SEM micrographs of W-OH and W-NCO samples. The images show changes on the fiber structure due to the reaction between the TDI and the wood surface. Particles on the fiber surface were observed after the reaction of wood macerated with TDI.

Fig. 2 shows the FTIR-PAS spectra of untreated wood samples, W-NCO, and W-NCO.

The band at 3341 cm^{-1} in the spectrum of macerated wood is sharper due to the axial deformation of free hydroxyls. The band in the region of $1000\text{--}1045\text{ cm}^{-1}$ was assigned to the symmetric >C-O stretching frequency of primary alcohol. The appearance of the band in the spectral region of $1720\text{--}1745\text{ cm}^{-1}$ after the reaction of wood with TDI (Fig. 2d) was corresponded to the >C=O stretching frequency of the urethane bonds, and the band at 2290 cm^{-1} was attributed to the free N=C=O groups. For this sample, the free isocyanate content was determined at 13.63%.

3.2. Polyol characterization

The polyols used in this work were characterized as to acidity and hydroxyl contents. These data were used in the calculation of the molar weight using Eq. (2). The results are given in Table 2.

$$M_n = \frac{2 \times 56.11 \times 1000}{I_{\text{OH}} + I_{\text{COOH}}} \quad (2)$$

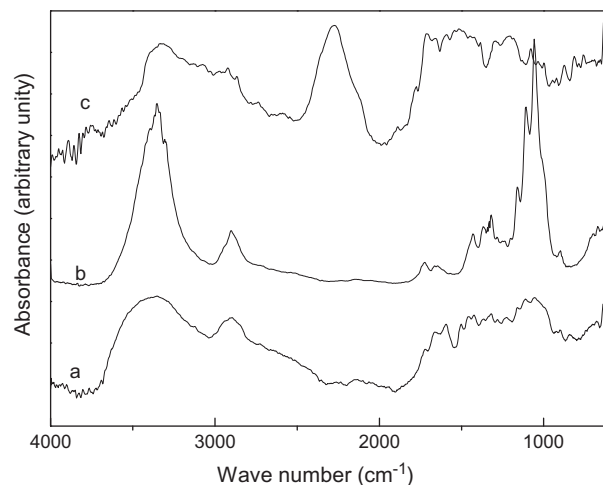


Fig. 2. FTIR-PAS spectra of: (a) untreated wood, (b) W-OH, and (c) W-NCO.

Table 2

Hydroxyl and carboxyl contents of PDG and commercial polyol PEG 4000.

Sample	I_{OH} (mg KOH/g)	I_{COOH} (mg KOH/g)	M_n (g/mol)
Poly(ethylene glycol) 4000	28	2.3	3700
PDG	120	4.6	905

where M_n is the numerical average molar weight, I_{OH} the hydroxyl content in mg KOH/g, and I_{COOH} is the acidity content in mg KOH/g.

3.3. Polyurethane/wood composites

3.3.1. FTIR-PAS analysis

The composites with different amounts of macerated wood presented a homogeneous aspect. Some compositions are shown in Fig. 3. It can be noticed that the samples have a uniform aspect

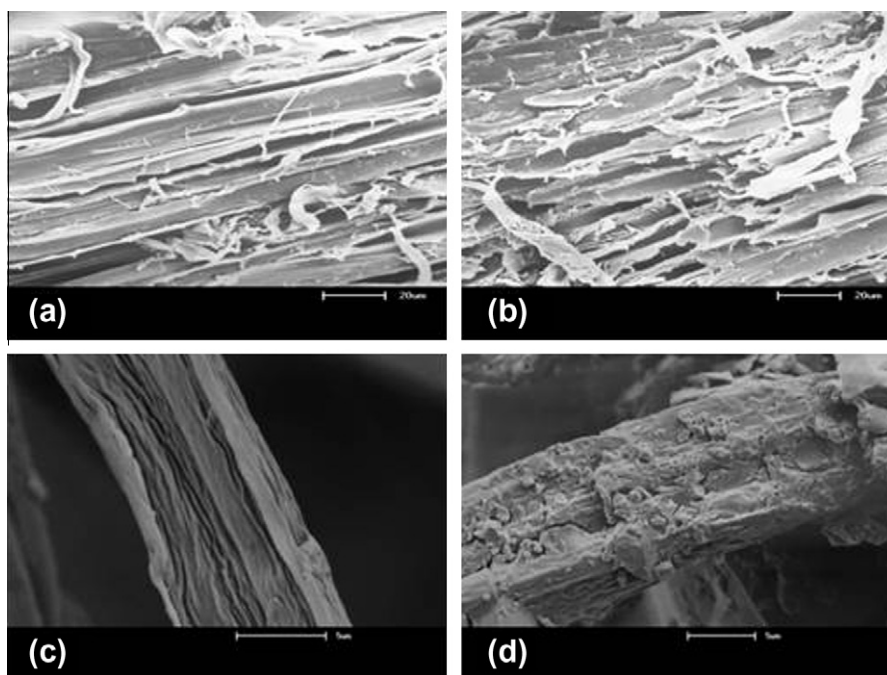


Fig. 1. SEM micrograph of: (a) untreated wood particles retained on the 0.42 mm sieves, (b) untreated wood particles retained on the 0.106 sieves, (c) W-OH, and (d) W-NCO.

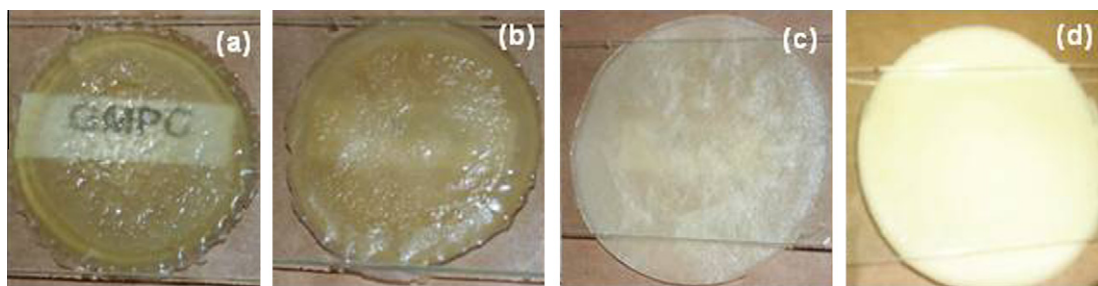


Fig. 3. Wood-polyurethane composites: (a) PU0, (b) PU7.5, (c) PU20, and (d) PU25.

and that the amount of macerated wood changes the material transparency.

The FTIR-PAS spectra of the composites with different mass fractions of wood are given in Fig. 4. The bands were assigned by the comparison of the characteristic frequencies of the molecule groups according to the literatures [23]. The intensity of the band at 2273 cm^{-1} , corresponded to the free $\text{N}=\text{C}=\text{O}$ stretching frequency, decreases with the increase in the wood mass fraction. All samples presented a band at 1720 cm^{-1} for the stretching of the carbonyl of the urethane bond and broadening of the band at approximately 3300 cm^{-1} due to the overlapping of the stretching bands of $\text{O}-\text{H}$ and $\text{N}-\text{H}$.

The proportion of polyols and isocyanate was kept constant, while the W-OH fraction of each sample was varied. The band relative to the free $\text{N}=\text{C}=\text{O}$ group (2273 cm^{-1}) decreased with the increase in the amount of wood in the composite. This decrease can be attributed to the formation of bonds between the free $\text{N}=\text{C}=\text{O}$ and the OH groups on the surface of the wood.

The band at 1535 cm^{-1} , attributed to $-\text{NH}-$ bending, reflects the total number of bonds between the OH groups issued from wood, PDG and PEG polyols, and the NCO groups issued from TDI. By normalizing the band at 1535 cm^{-1} with respect to the band at 2880 cm^{-1} ($>\text{CH}-$ stretching frequency), the differences on the thickness of the samples could be corrected. Such normalization, defined as $R = A_{1535}/A_{2880}$, was calculated by the ratio between the intensity of the band at 1535 cm^{-1} and the intensity of the band at 2880 cm^{-1} . Table 3 shows the R values of composite samples. The R values were expected to increase with increasing wood composition. However, this was not observed for both

Table 3

R values of composite samples obtained from FTIR.

Sample	PU0	PU7.5	PU10	PU15	PU20	PU25
$R = A_{1535}/A_{2880}$	0.37	0.39	0.44	0.48	0.45	0.27

PU7.5 and PU25 samples. These results were obtained on basis of SEM micrographs and mechanical analyses.

3.3.2. SEM analysis

SEM micrographs of polyurethane/wood composites with varying amounts of macerated wood fractured in liquid nitrogen are presented in Fig. 5A–E. The SEM images show two opposite morphological situations: (a) domains of fibers dispersed in the polyurethane matrix and a significant interfacial interaction between the fiber and the polymer (indicated by the arrows) can be observed for PU7.5, PU10, PU15 and PU20 (Fig. 5A–D), which prevents the fiber release from the polymer matrix, and (b) poor interfacial interaction between the fibers and the polymer that contributes for the fiber release from the polymer matrix, observed for PU25 (Fig. 5E). There may not be adherence due to the increase in the amount of the wood in the composites. We can infer that the interaction between the phases is the result of the bonds of polyols with the NCO groups of the TDI, which are covalently bonded to $-\text{OH}$ groups on the wood surface. Although the composites contain the same amount of TDI and polyols, in sample PU25 the amount of TDI is not sufficient to react with all W-OH in the medium, contributing to reduce the amount of polyols covalently bonded to surface wood and consequently the interaction between the phases.

3.3.3. Mechanical tests

The mechanical behavior of composites PU7.5, PU10, PU15, PU20, and PU25 with respect to PU0 can be verified in Fig. 6. The relative values of properties were obtained by the ratio between the composite properties and the PU0 properties. The relative Young's modulus and the relative tensile strength of the composites PU10, PU15, and PU20 are higher than those of the PU0. To these compositions, the increase in the values of maximum tensile strength and Young's modulus indicates a significant interfacial interaction between the fiber and the polymer matrix, shown in the SEM micrographs. The composite PU10 presented the maximum values of relative Young's modulus and relative maximum tensile strength of 21.2 MPa and 3.74 MPa, respectively.

The mechanical behavior of both the PU0 and the composites in the stress-strain tests can be seen in Fig. 7. The stress-strain curves of PU0 and of composites PU7.5, PU10, PU15, and PU20 are typical of ductile material. The after-assay length of these samples was greater than the initial length, demonstrating the plastic elongation of the material; however, narrowing did not occur. The curve of composite PU25 is more similar to that of a brittle material, and the final length is similar to the initial length. The

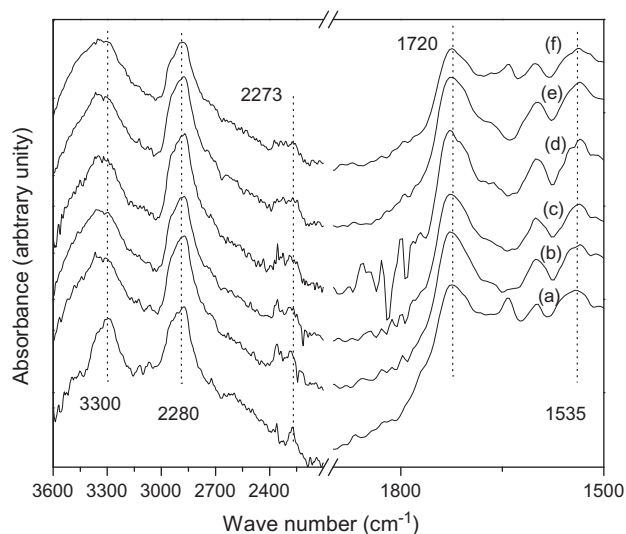


Fig. 4. FTIR-PAS spectra of polyurethane/wood composites: (a) PU0, (b) PU7.5, (c) PU10, (d) PU15, (e) PU20, and (f) PU25.

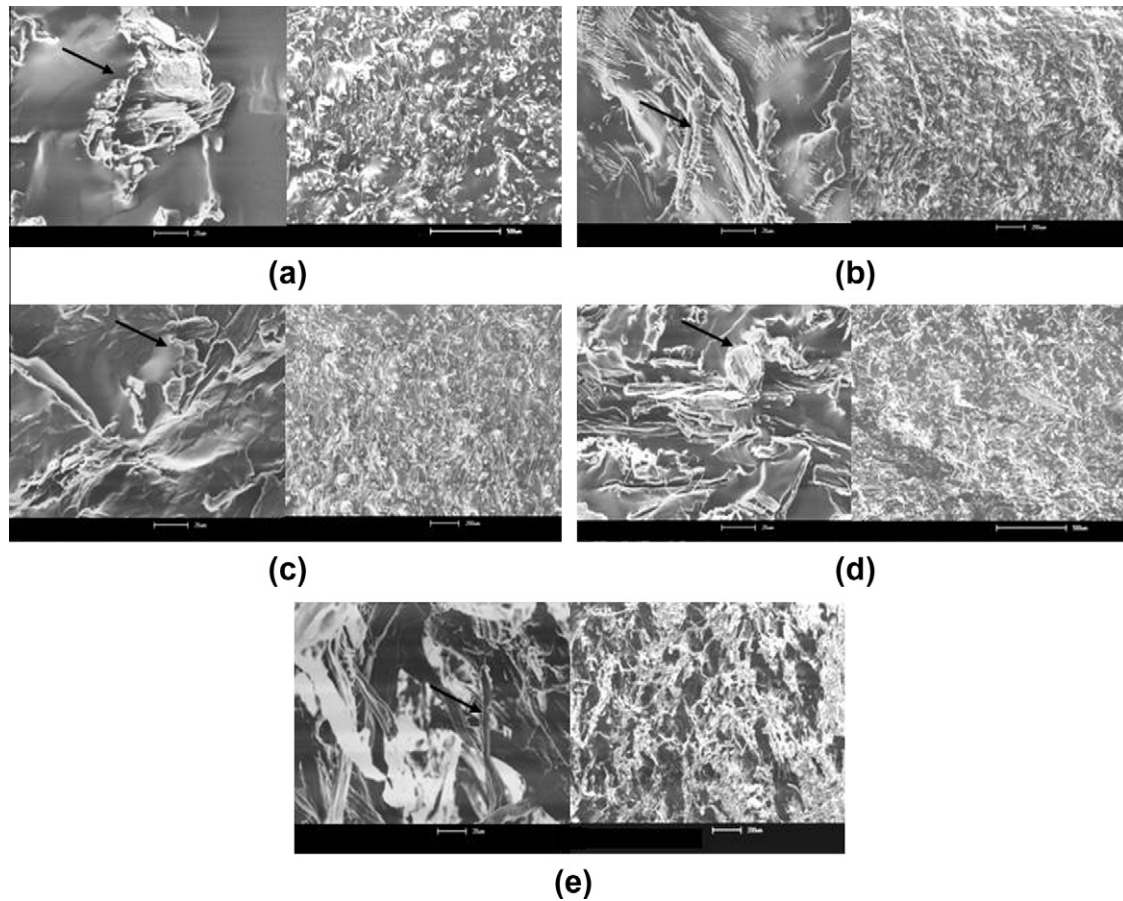


Fig. 5. SEM micrographs of polyurethane/wood composites: (A) PU7.5, (B) PU10, (C) PU15, (D) PU20, and (E) PU25.

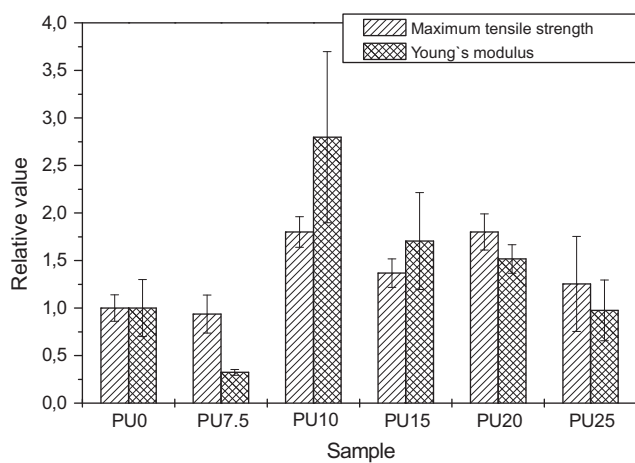


Fig. 6. Relative tensile strength and relative Young's modulus of PU/wood composites with respect to PU0.

Young's modulus of this composite is smaller than those of the other composites, indicating a smaller interaction between the phases.

The interface plays an important role in the mechanical properties of composite materials, as that is where load transfer from the matrix to the dispersed phase occurs.

The load transfer from the polymer matrix to the dispersed phase in the composites PU10, PU15, and PU20 is more effective,

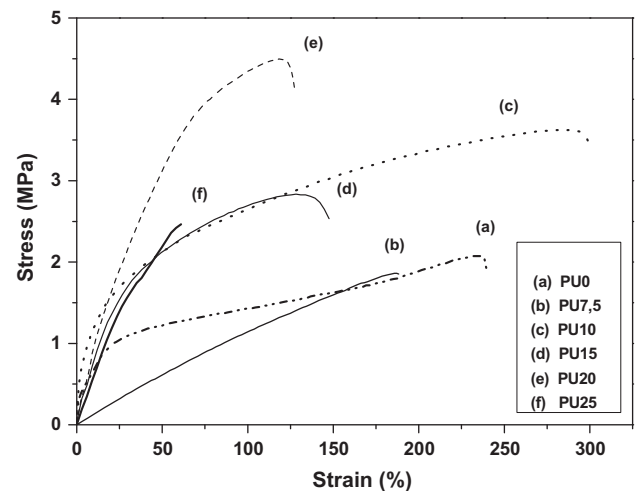


Fig. 7. Stress-strain curves of PU and PU/wood composites.

which increases the elasticity modulus and the maximum tensile strength in relation to those of PU0. The load transfer was less effective in the composites with 7.5% and 25% of wood.

FTIR analyses of sample PU25 showed that the R value is lower than the samples containing smaller amount of wood. Furthermore, SEM micrographs (Fig. 5F) showed that part of the wood is not adhered to the polymer matrix. These results corroborate the mechanical analysis, strengthening the argument that the amount

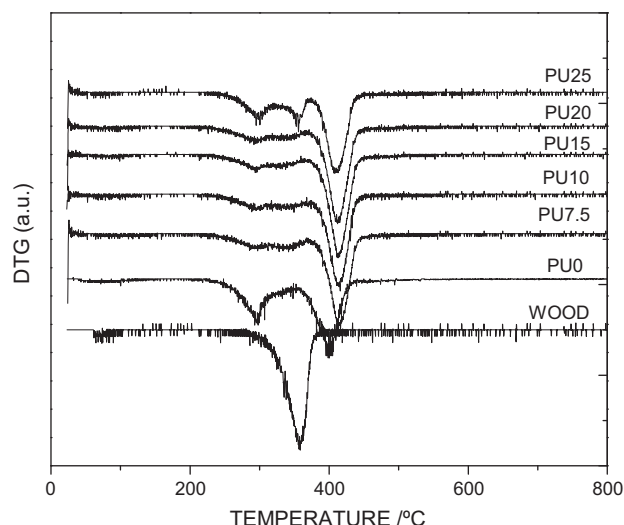


Fig. 8. DTG curves of macerated wood and polyurethane/wood composites.

Table 4

Onset (T_o) and maximum (T_{max}) temperatures of the two decomposition steps of composites and macerated wood.

Sample (PU/wood)	Step	T_o (°C)	T_{max} (°C)
PU0	1	230	294
	2	359	399
PU7.5	1	239	294/339
	2	372	415
PU10	1	232	297/332
	2	365	412
PU15	1	245	296
	2	372	413
PU20	1	239	296
	2	372	413
PU25	1	246	299
	2	332	354
	3	377	410
Macerated wood	1	281	357

of wood is not sufficient to react with all the wood in the medium. As a result, the phase interaction and the load transfer are less effective for this sample.

Mechanical results for sample PU7.5 suggested poor adhesion between the phases. We suggest that the reaction of polyols and NCO can be processed by a two-way reaction. In the first way, there may be heterogeneous reaction between the polyols (liquid phase) and the W-NCO (solid phase) (diffusion controlled). In the second way, there may also be a homogeneous reaction between the polyols and the TDI (liquid phase). The heterogeneous reaction is slower than the homogeneous reaction because it is a reaction that requires diffusion of polyols onto the surface of W-NCO. For sample PU7.5 it is supposed that the homogeneous reaction probably occurs rather than the heterogeneous reaction, in view of the small amount of wood. Therefore, the sample PU7.5 exhibits reduced values of both the Young's modulus and the tensile strength, compared with the other compositions and the same R value (Table 2) of the sample PU0.

The heterogeneous reaction rate is related to the amount of wood composite, because the increase of the wood increases the number of W-NCO groups available to establish interactions with molecules of polyols. For the samples PU10, PU15 and PU20, a part of polyols may be covalently bonded to surface W-NCO and another part of polyols may be reacted with the TDI, thus forming a more effective interaction between the phases.

We can observe higher values of both Young's modulus and tensile strength for the sample PU10, indicating that the wood proportion of 10% is a threshold value for a good mechanical performance, performance begins to decrease. So, for the composites with more than 10% of wood, we can infer that the heterogeneous reaction is controlled by diffusional process. Thus the number of W-NCO-bonding polyol molecules decreases as the amount of wood increases.

3.3.4. Thermogravimetric analysis

The thermal stability of PU0 and composites is an important parameter for end-use product application. Therefore, TGA was conducted in order to assess the effect of different weights of macerated wood on the thermal properties of composites. Derivative thermogravimetric curves (DTG) of polyurethane/wood composites, pure polyurethane, and macerated wood are shown in Fig. 8. The pure polyurethane and the composites presented a two-step decomposition process, while macerated wood presented only one-step. The first decomposition step of the composites, between 230 and 380 °C, corresponds to the decomposition of the urethane groups and wood. The second step, between 360 and 460 °C, corresponds to the decomposition of the polyol segments. The maximum weight loss temperature (T_{max}) of the first decomposition step in the DTG curve increased only slightly with the increase in the amount of wood in the composite above 7.5% wood (m/m) and the onset decomposition temperatures (T_o) did not vary significantly in this step. In the second decomposition step, both T_o and T_{max} increased slightly with the increase in the amount of wood in the composites (Table 4), indicating no significant improvement of the thermal stability of the material due to the presence of wood.

4. Conclusions

The maceration of industrial wood wastes with peracetic acid exposes wood-surface hydroxyl groups and allows their reaction with $N=C=O$ groups of the TDI. The polyols obtained by chemically recycled PET proved to be viable for the synthesis of the polymer matrix.

Polyurethane/wood composites were produced using chemically modified furniture industry wood wastes and polyols obtained from chemically recycled PET. FTIR-PAS analysis of the wood fibers and the composites indicated the reaction of fiber surface groups with TDI. This reaction affords adhesion between the polymer and the wood since the polymer matrix is partially, covalently bonded to wood surface, contributing to form a more effective interaction between the phases, and load transfer from the matrix to the dispersed phase. The covalent bonds between the W-NCO and the polyols result in increased tensile strength and Young's modulus, which were maximum in the composite with 10% wood (m/m), (3.6 MPa and 21.2 MPa, respectively). The wood proportion of 10% is a threshold value for a good mechanical performance. The morphological analysis of cryofractured samples by SEM showed adhesion between the phases for composite PU7.5; PU10; PU15 and PU20. TGA analysis indicated no significant improvement in thermal stability of the composites, compared with that of the pure polyurethane.

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